

Remarks

Consideration of this application in view of the above amendments and following remarks is respectfully requested. Claims 1, 8-10 and 20-28 are now pending. Claims 2-7 and 11-19 have been canceled. Claims 1 and 8-10 have been amended. Claims 20-28 are new.

Priority Claim

This application is a continuation of U.S. Application No. 09/198,323 filed November 24, 1998 (hereinafter “the parent application”). Priority to U.S. Application No. 08/520,333 filed August 25, 1995 (which issued as U.S. Patent No. 5,840,438) is no longer being claimed in this continuation application.

Applicability of 35 U.S.C. §103(c)

This application, having been filed after November 29, 2000, is subject to the “safe harbor” provisions now afforded by 35 U.S.C. §103(c) with regard to potential 35 U.S.C. §102(e) prior art. Accordingly, U.S. Patent No. 5,840,438 to Johnson et al. (hereinafter “the ‘438 patent”) may no longer serve as §102(e) prior art under §103(c) since both the ‘438 patent and the claimed subject of this application were, at the time the invention was made, owned by the same person, or subject to an obligation of assignment to the same person (*i.e.*, Ballard Power Systems).

Allowability of New Claims 20-28

By final Office Action mailed September 17, 2001 in the parent application, the Examiner indicated that claims 2, 7, 12-17 and 19 contained allowable subject matter, but stood objected to for the reasons of record. To expedite issuance of these claims, Applicants have added new claims 20-28 as discussed below.

At no time during prosecution of the parent application had claims 16-17 been rejected. Thus, Applicants have added new independent claim 20 to parallel claim 16, added new dependent claim 21 (which depends from claim 20) to parallel claim 17, and cancelled claims 16-17.

Similarly, the Examiner indicated that claims 2, 7, 12-15 and 19 also constitute allowable subject matter. Thus, Applicants have added new claims 22-28 which recite these

allowed claims in independent format, and have cancelled claims 2, 7, 12-15 and 19. More specifically, new claim 22 corresponds to allowable claim 2, new claim 23 corresponds to allowable claim 7, new claims 24-27 correspond to allowable claims 12-15, and new claim 28 corresponds to allowable claim 19.

Accordingly, allowance of claims 20-28 is respectfully requested.

Rejection of Claims

By final Office Action mailed September 17, 2001 in the parent application, (a) claims 1, 5, 11 and 18 stood rejected as obvious over U.S. Patent No. 5,702,839 to Frost *et al.* in view of U.S. Patent No. 5,958,613 to Hamada *et al.*; (b) claims 1, 6 and 8 stood rejected as obvious over JP 10-92439 in view of Hamada *et al.*; and (c) claims 1, 3, 4, 6, 9 and 10 stood rejected as obvious over JP 3-222261. Applicants respectfully traverse these rejections for the reasons set forth below.

As an initial matter, and in order to expedite allowance of certain aspects of this invention, Applicants have canceled rejected claims 3-5, 11 and 18. Of course, Applicants reserve the right to continue prosecution of the canceled subject matter in one or more related applications.

In addition, Applicants have amended claim 1 by inclusion of the text of claim 6. In other words, claim 1 has been amended to recite that the fluid transport properties of the first electrode substrate vary as it is traversed in-plane in the direction of the first reaction flow path. In view of this amendment, claim 6 has been canceled and claims 8, 9 and 10 have been amended to depend from claim 1 (as opposed to canceled claim 6).

The only rejections that had been applied to claim 6 in the parent application involve rejections “(b)” and “(c)” above – that is, the rejection of claim 6 as obvious over JP 10-92439 in view of Hamada *et al.*, and as obvious over JP 3-222261. Applicants respectfully traverse these grounds of rejection as applied to amended claim 1 (and claims 8-10 which depend therefrom) for the following reasons.

Rejection Based on JP 10-92439 in view of Hamada *et al.*

JP 10-92439 is published in the Japanese language. However, this patent is a member of a patent family that contains English language equivalents. One such equivalent is GB 2316802 (a copy of which is submitted herewith, along with the DIALOG[®] printout showing it to be a member of this family). Thus, all further reference to this patent will be to GB 2316802 (hereinafter “GB 802”).

GB 802 is directed to a gas diffusion electrode having:

an anisotropic gas diffusion layer that is made of a porous carbon matrix through which carbon particles and polyethersulfone are distributed such that the matrix is homogeneously porous in a direction lateral to gas flow and asymmetrically porous to gases in the direction of gas flow, the porosity of the gas diffusion layer decreasing in the direction of gas flow, ...

See GB 802 at page 10, lines 15-21 (emphasis added).

In the Office Action issued in the parent application, the Examiner understood the above language to teach that “the porosity of the substrate is ‘lowered’ toward the end of the gas flow.” (9/17/01 Office Action at page 3). This is opposite to what GB 802 actually teaches. Rather, the porosity of the GB 802 matrix is *homogenous* as it is traversed in-plane to the direction of the reactant flow path, and *asymmetrical* through the matrix. Confusion regarding this point appears to lie in the phrases “lateral to gas flow” and “direction of gas flow”. As used in claim 1 of the pending application, the phrase “direction of gas flow” means from the first port to the second port such that the flow path extends in-plane across the electrochemically active area. In contrast, the phrase “direction of gas flow” as used in GB 802 means gas flow through the electrode matrix, from one face to the other.

This direction of flow is evident upon reference to page 22, lines 7-16, of GB 802. This portion of GB 802 clarifies that the direction of gas flow, after entering the electrode, is through the less resistant surface and toward the more dense portion of the matrix. Thus, as stated at page 22, lines 13-15, “the electrode matrix of the [GB 802] invention has an anisotropic porous structure with two asymmetric surface layers ...” These asymmetric surface layers yield a matrix that is “asymmetrically porous” to gases in the direction of gas flow (*i.e.*, through the matrix), but “homogeneously porous” in the direction lateral to gas flow (*i.e.*, across the matrix).

As the Examiner will appreciate, this is directly contrary to the subject matter recited in claim 1 with regard to flow across the matrix.

Therefore, GB 802 does not teach or suggest the invention as recited in claim 1. The addition of Hamada *et al.* does not cure this deficiency since it is entirely silent on the issue.

Accordingly, Applicants respectfully submit that amended claim 1, as well as dependent claims 8-10, are patentable in view of GB 802, and request that this ground of rejection be withdrawn.

Rejection Based on JP 3-222261

As with the Japanese patent document discussed in the prior section, JP 3-222261 is also in the Japanese language. Since Applicants were unable to locate an English language equivalent of this document, an English language translation has now been obtained. A copy of the translation is submitted herewith, and all further reference to JP 3-222261 will be to the English language translation (hereinafter “JP 261”).

As an initial matter, JP 261 is directed to a solid electrolyte (*e.g.*, stabilized zirconia) fuel cell that is quite different, in both principle and operation, from the membrane or polymer electrolyte fuel cell (PEFC) of this application. Thus, Applicants respectfully submit that, although the disclosure of JP 261 is to a “fuel cell”, it does not constitute analogous art to a PEFC. For example, a PEFC typically operates at a temperature of about 80°C, while a solid electrolyte fuel cell (such as that disclosed in JP 261) has typical operating temperatures ranging from 800 – 1,000°C. Further, in a solid electrolyte fuel cell, mass-transfer conditions may largely be ignored due to the higher reactant and product diffusivities.

With these differences in mind, the problem to be solved in JP 261 had to do with thermal stress attributable to heat (due to uneven current) being produced in a nonuniform manner which, in turn, was caused by an abundance of fuel near the fuel gas inlets and shortage of fuel near the outlets (*see* JP 261 at bottom of page 5 and top of page 6). To solve this problem, the “fuel electrode” (*i.e.*, the anode) purportedly had an area of low porosity near the fuel inlets (*see* Figure 2 of JP 261). By designing the anode in this manner uniform temperature distribution could be obtained, thus providing the solid electrolyte fuel cell extended life and other benefits noted in JP 261 (*see* top of page 10).

As the Examiner will appreciate, the problems inherent in a solid electrolyte fuel cell do not necessarily present themselves in a PEFC. In particular, the thermal uniformity that was sought in the JP 261 patent is not necessarily advantageous in a PEFC. Rather, in a PEFC water management on the cathode side of the membrane electrode assembly (MEA) is important in avoiding performance loss, and such fuel cells are beneficially operated with a temperature gradient increasing from the inlet port to the outlet port. As a consequence, the additional water produced along the path from the inlet to the outlet is mitigated by the increased amount of water vapor that the stream can carry due to the temperature rise (*see* paragraph spanning pages 103-104 and Figure 6 in St-Pierre et al., “Relationships Between Water Management, Contamination and Lifetime Degradation in PEFC,” *J. New Materials for Electrochem. Systems* 3:99-106, 2000) (copy attached). Thus, maintaining a temperature gradient is actually a desired attribute in the design of the cathode for a PEFC for reasons related to mass transport, while the solid electrolyte fuel cell of JP 261 sought to eliminate any such temperature gradient by modification of the anode.

To further clarify this distinguishing feature, Applicants have amended claim 1 to recite that “said first electrode is a cathode.” By this amendment, claim 1 recites that the fluid transport properties (*e.g.*, porosity) of the first electrode – that is, the cathode - vary as it is traversed in-plane in the direction of the first reactant flow path. This aspect of claim 1 is not taught or suggested by JP 261. Furthermore, one skilled in this field would not be motivated to make such a modification since the very reason for lowering porosity near the fuel inlet in JP 261 was to yield uniform temperature distribution, as opposed to addressing mass transport considerations at the cathode of a PEFC.

Accordingly, Applicants respectfully submit that claim 1, as well as dependent claims 8-10, are patentable over JP 261 and request that this ground of rejection also be withdrawn.

Attached is a Supplemental Information Disclosure Statement, along with completed PTO Form 1449, listing the references identified and discussed herein.

Also attached hereto is a marked-up version of the changes made to the specification and claims by the current amendment. The attached page is captioned “**Version With Markings to Show Changes Made.**”

In view of the above amendment and remarks, allowance of claims 1, 8-10 and 20-28 is respectfully requested. A good faith effort has been made to place this application in condition for allowance. However, should any further issue require attention prior to allowance, the Examiner is requested to contact the undersigned at (206) 622-4900 to resolve the same.

Respectfully submitted,

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VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Claims:

Claims 2-7 and 11-19 have been canceled.

Claims 1 and 8-10 have been amended as follows:

1. (Amended) An electrochemical fuel cell assembly comprising:
 - a first separator plate having a pair of oppositely facing major planar surfaces, and first and second ports;
 - a second separator plate having a pair of oppositely facing major planar surfaces, and third and fourth ports;
 - a membrane electrolyte interposed between said first and second separator plates;
 - a first electrode interposed between said first plate and said membrane electrolyte, said first electrode comprising a first substrate having a pair of oppositely facing major planar surfaces and electrocatalyst associated therewith defining a first electrochemically active area; and
 - a second electrode interposed between said second separator plate and said membrane electrolyte, said second electrode comprising a substrate having a pair of oppositely facing major planar surfaces and electrocatalyst associated therewith defining a second electrochemically active area;
- said electrochemical fuel cell assembly further comprising a first reactant flow path for directing a first reactant fluid stream between said first and second ports, wherein said first reactant flow path extends substantially linearly across said first electrochemically active area, and a fluid transport property of said first electrode has an in-plane nonuniform structure in its electrochemically active area as said active area substrate varies as it is traversed in-plane in the direction of said first reactant flow path, and wherein said first electrode is a cathode.
8. (Amended) The electrochemical fuel cell assembly of claim 1 [6] wherein the density of said first electrode substrate increases as it is traversed in-plane in the direction of said first reactant flow path.

9. (Amended) The electrochemical fuel cell assembly of claim 1 [6] wherein the porosity of said first electrode substrate increases as it is traversed in-plane in the direction of said first reactant flow path.

10. (Amended) The electrochemical fuel cell assembly of claim 1 [6] wherein the pore size of said first electrode substrate increases as it is traversed in-plane in the direction of said first reactant flow path.

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Relationships between water management, contamination and lifetime degradation in PEFC

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Abstract: Water management in PEFCs is an important parameter to optimize for peak performance. Its importance is further emphasized by data obtained with impurity-contaminated cells and from life tests carried out using several cell humidification levels. The results show the detrimental effects of impurities on several key cell performance loss types (including kinetic, ohmic and mass transport losses). Furthermore, an improper water balance (either too wet or too dry) has a long term effect on cell degradation rates. Efficient and practical water management strategies to reduce the detrimental effects of impurities and exposure to excess water or dryness are also reviewed.

Key words: Polymer electrolyte fuel cells, cell performance, water management, contamination, degradation.

1. INTRODUCTION

Proper water management is paramount in polymer electrolyte fuel cells (PEFCs) since performance losses could result due to cathode flooding, gas dilution or membrane dehydration. In a previous paper [1], three water management strategies were discussed (pressure drop, temperature rise, counterflow operation) with an emphasis given to cell performance and operation under zero humidification. These methods are easy to implement and were found to reduce mass transport limitations due to water management especially at high current densities and low oxidant stoichiometries. Membrane dehydration was not an issue and these approaches can reduce or eliminate the need for humidification.

However, other substantial benefits are gained using proper water management strategies. For example, the presence of excess water can negatively affect cell performance by transporting leached impurities within the cell, subsequently depositing them on catalysts or the membrane where they modify electrode performance or the electrolyte ionic conduction mechanism

leading to increased ohmic and mass transport loss. Even in the absence of impurities, prolonged exposure of the membrane/electrode assembly (MEA) to excess water may also result in a permanent loss of performance attributed to material degradation.

In this paper, the effect of impurities will first be discussed. The discussion will be followed by a brief account of effective water management strategies demonstrated at Ballard, which can mitigate or reduce impurity effects. The importance of effective water management to achieve acceptable fuel cell durability will also be shown in the last section by ex-situ tests and with operating cells both conducted for at least 1000 hours.

2. EXPERIMENTAL

Standard Ballard Mk5 and Mk513 fuel cells and fuel cell stacks were used. Whereas the Mk5 stack was operated isothermally to the extent possible, the Mk513 stack was operated with a temperature gradient between the inlet and outlet coolant ports. Standard Ballard test equipment (external humidifier, gas mixer, test station and electronic load) that controls gas type and composition, flows, pressures, relative humidities, temperature and cell current density were also used. Commercial multimeters, milliohmmeters and thermometers completed the array of

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equipment required to obtain polarization curves, reformat diagnostics and lifetime data.

Purposeful MEA contamination was obtained by soaking N117 Nafion® membranes for 16 hours at room temperature in $\text{Fe}_2(\text{SO}_4)_3$ solutions (0.1, 0.19, 0.33 M). The treated membranes (23 cm by 23 cm) were subsequently rinsed several times with deionized water to remove any excess iron. Small membrane samples were cut to determine the iron content whereas the remainder was bonded into an MEA. The membrane samples were vacuum dried at 70 °C and digested in nitric acid contained in a Parr bomb. The supernatant was analyzed by ICP-MS. The membrane iron concentration was computed by assuming that each Fe^{+3} was associated with three sulfonate sites. The contaminated MEAs were conditioned overnight before measurements were completed. However, it should be noted that the MEA which has a sulfonate site loss of 100 % (all sulfonate site groups are associated with Fe^{+3}) initially had an open circuit voltage close to 0. The open circuit voltage gradually increased with wet oxidant and fuel circulation to a point where operation was possible. The contamination is therefore, at least partially, a reversible process.

3. RESULTS AND DISCUSSION

3.1. MEA contamination

Fundamental studies addressing the properties of membranes containing different cations [2-11] and catalyst surface area loss in phosphoric acid [12] offer a good basis to understand impurity effects on MEA performance.

With respect to Nafion® properties, previous measurements reported in the literature were carried out using an array of different methods (quartz crystal microbalance, impedance spectroscopy, streaming potential, electrophoresis, four probe dc potential) [2-11] revealed that foreign cations in general, such as alkali metals (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+), alkaline earths (Mg^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2}), transition elements (Ag^+ , Ni^{+2} , Mn^{+2} , Cu^{+2} , Zn^{+2} , Cr^{+3}), rare earths (La^{+3}), Al^{+3} and ammonium derivatives ($\text{R}_n\text{NH}_4^{n+}$ where $\text{R} = \text{H}$, CH_3 , C_2H_5 , C_3H_7 , C_4H_9 and $n = 0$ to 4), will enter the membrane by displacing H^+ ions and decrease its conductivity proportionately to the cation ionic charge. This is explained by the variation of the interactions between the mobile ions, water dipoles and the fixed sulfonate sites, which are related to the cation hydration radius, the relative ion and channel diameter size, and the membrane microstructure. The reduced conductivity is partly explained by the simultaneous expulsion of water molecules (reduction of 0.7 to 12 from 21 $\text{H}_2\text{O}/\text{SO}_3\text{H}$ for Nafion in acid form) when H^+ is exchanged with other cations [2]. As a result of this exchange, electrostatic cross-linking or formation of sulfonate salts can occur, which causes retraction of the membrane, thus squeezing water out, and decreases ionic conductivity. The lower water content may explain why the water diffusion coefficient is reduced, since steric hindrance will increase due to membrane shrinkage. The lower diffusion coefficients are also partly explained by the intrinsically lower values for alkali metal cations (different transport mechanism

than for H^+). Cations entering the membrane also have an effect on the water transference coefficient (electroosmotic drag). Values of 5.2 to 15.6 were found for alkali metal and alkaline earth cations which are much larger than 2.6 for the acid form of Nafion and is therefore indicative of a different mechanism at play for H^+ transport. The larger water transference coefficients with foreign cations imbedded in the membrane was rationalized by two mechanisms: charge-dipole interactions (hydration water) and cation size (pumping effect exerted by moving cations) [13].

All the previous cation effects (decreased membrane conductivity and water diffusion coefficient, increased water transference coefficient) have a direct impact on MEA performance because they can lead to much faster or more extensive membrane dehydration especially near the anode. This will in turn lead to a larger mass transport loss, and ohmic drop loss (which is already increased by the lower membrane conductivity). Furthermore, it was also demonstrated by a modelling approach that the impurity effect on MEA performance is dependent on the location of the contaminants (a uniform distribution across the thickness of the membrane is less severe than concentration near the anode which in turn is less severe than concentration near the cathode)[8].

With respect to the catalyst, cyclic voltammetry measurements performed in phosphoric acid [12] revealed that the cathode PtCrNi alloy (2:1:1 ratio) surface area decreases with time (100 hours) at low potentials (0.1 V vs RHE). If the potential was subsequently increased, the active surface area was recovered. These results were explained by the presence of electrolyte impurities that undergo adsorption or desorption at the catalyst surface depending on the potential value. Similar phenomena are likely possible in PEFCs (anode or cathode) and may be even more probable because of the lower operating temperature. Impurity adsorption would lead to increased kinetic losses at all current densities.

In the remainder of this section, data obtained at Ballard will be presented that will confirm the conclusions obtained from the literature survey. Fig. 1 illustrates polarization data obtained with MEAs contaminated to different levels with iron. In all regions of the polarization curves (kinetic, ohmic, mass transport) substantial losses are observed which correlate well with the conclusions obtained from the literature analysis. The losses are readily quantifiable using the following equation [14] to fit the polarization data with oxygen of Fig. 1:

$$E = E_0 - b \log i - Ri \quad (1)$$

$$E_0 = E_i + b \log i_0 \quad (2)$$

where E is the cell voltage, b and i_0 are respectively the Tafel slope and exchange current density for the oxygen reduction reaction, i is the current density, R is the ohmic area resistance and E_i is the reversible potential. Kinetic losses are increased by contamination resulting in increased b but lower E_0 values (Table 1). Changes in the ohmic loss are not observed partly due to insufficient data for the MEA which has a sulfonate site loss of

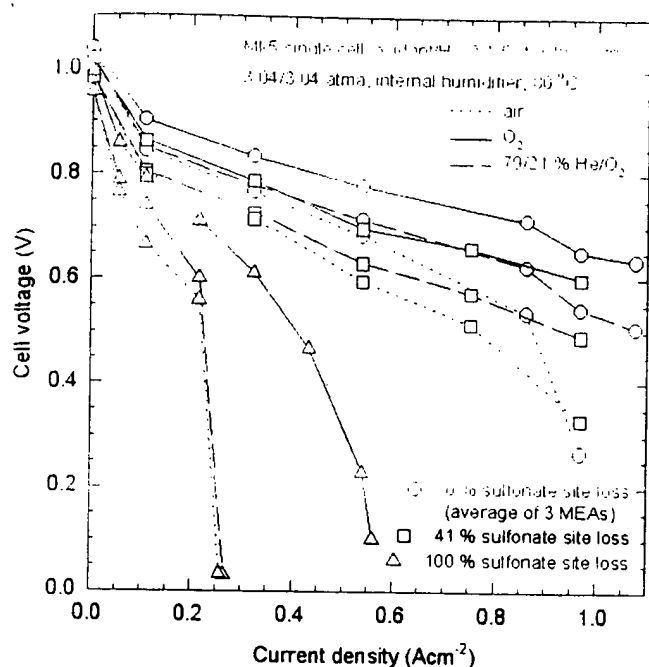


Fig. 1. Effect of iron contamination at three different levels on MEA performance with three different oxidants (oxygen, helox, air).

Table 1. Parameters derived from the iron contaminated MEA oxygen polarization data (Fig. 1)

Contamination level (% of sulfonate sites associated with iron ions)	0	41	100***
E_0 (V)	0.864	0.799	-
b (Vdecade ⁻¹)	0.070*	0.091	-
R (Ω cm ²)	0.205	0.207	-
Limiting current** (Acm ⁻²)	≈ 1	≈ 1	0.25

* assumed value

** from air data

*** insufficient data for accurate estimation

100 %. Smaller limiting current densities observed under air operation are indicative of increased mass transport losses.

Contamination can also affect anode reformat tolerance. Fig. 2 illustrates the corresponding cell voltage as a function of the air bleed value used to deal with the CO (10 ppm) and CO₂ in the fuel stream. The intrinsic CO tolerance (0 % air bleed) is 0.57 V and very little air is required to eliminate the CO effect (0.5 % air bleed). The voltage difference between hydrogen and reformat operation is at that point 27 mV and is due to dilution, and the poisoning effect of CO₂ [15]. With an iron contaminated MEA (41 % of sulfonate sites associated with iron ions), the intrinsic CO tolerance drops to 0.34 V. In addition, a much larger amount of air is required (> 10 % air bleed) to substantially eliminate the

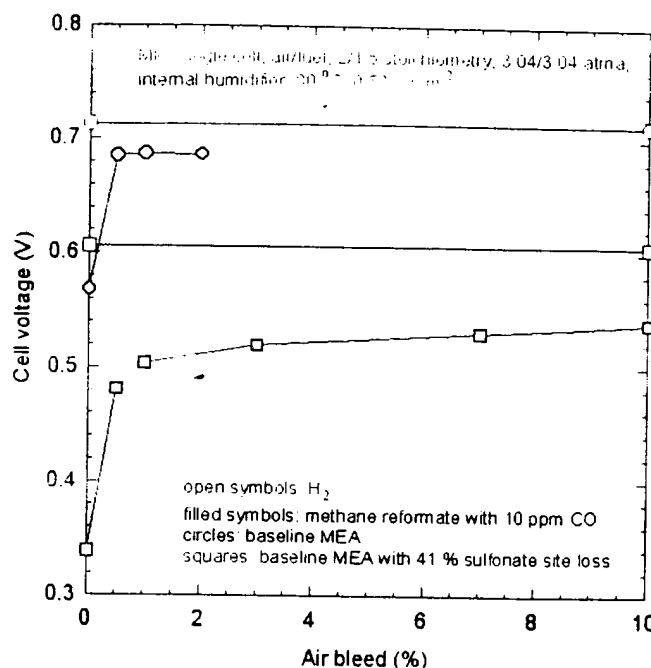


Fig. 2. Effect of iron contamination on MEA performance with reformat at different air bleed levels.

CO effect. Even at a 10 % air bleed, the voltage difference between hydrogen and reformat operation is still 60 mV which is substantially larger than the 27 mV obtained in the absence of MEA contamination. All of this reveals the significant effect contaminants can have on the anode performance.

It is clear that contamination of the MEA can have a significant effect on cell performance. Ideally, measures such as good water management should be taken to protect all MEA materials from contamination.

3. 2. Effective water management strategies

Excess water can carry contaminants to sensitive areas of the MEA by several routes. For example, excess water can transport contaminants located upstream in the system or can leach contaminants out of the fuel cell stack or system components. As a result of these processes, as discussed in the previous section, excess water can lead to several types of performance loss with contamination (kinetic, ohmic, mass transport). Optimum cell performance therefore relies on the ability to control the cell water balance to the desired level. The literature contains many references related to water management within PEFCs (references cited in [1] and [4,13,16-44]). However, many water management strategies previously reported do not possess the characteristics required for practical PEFC systems such as reliability and ease of implementation. Some of the methods developed at Ballard to achieve an appropriate water balance may be broadly classified into two groups: flow field/operational conditions [1] and MEA design [45]. In the former case, techniques involving control of pressure drop and coolant temperature gradients, and reactant gas counterflow operation were demonstrated [46-48], whereas in the

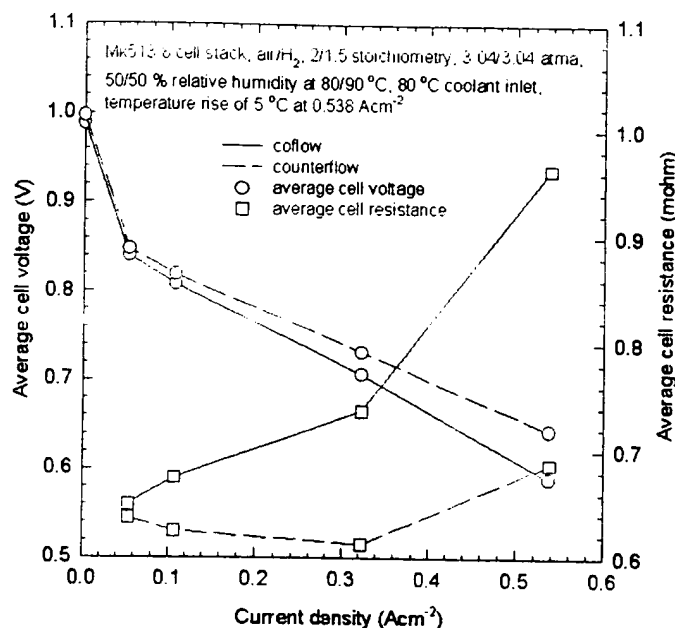


Fig. 3. Effect of cell operation mode on MEA performance and resistance.

latter case, strategies involving the electrode substrate structure and catalyst distribution have also shown benefits [49-51]. Some results are reported here to demonstrate the effectiveness of these water management strategies.

Fig. 3 and 4 respectively show results obtained using reactant gas counterflow operation with the coolant and oxidant in co-flow (flow field/operational condition approach) and a modified substrate structure (MEA design approach). With a gas counterflow operation mode and less than 100 % relative

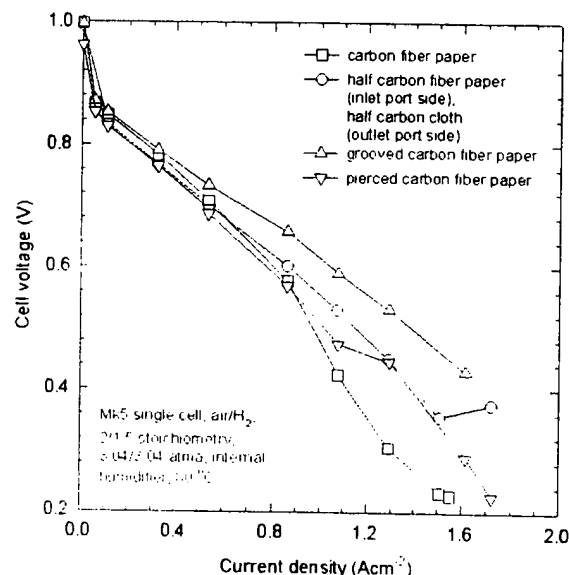


Fig. 4. Effect of the electrode substrate structure on MEA performance.

humidity for both streams, better water redistribution within the cell is achieved since the relatively wet oxidant outlet is partly relieved by the lower relative humidity inlet fuel. In addition, the water added to the fuel is transported towards the oxidant inlet (fuel outlet), which in turn may relieve its relative dryness. However, for water saturated reformat cases, only the dry air inlet benefits from the counterflow operation water management strategy. The gas counterflow operation mode with a coolant temperature rise is particularly beneficial under low relative humidities as both the polarization curves and cell resistances of Fig. 3 demonstrate. The smaller slopes obtained at high current densities for the polarization curves are indicative of the smaller membrane resistance due to the better water distribution. This conclusion is also supported by the cell resistance measurements.

The performance loss associated with water accumulation and flooding in the cell as a function of position along the oxidant flow field can also be reduced by modifying the MEA. Since water accumulation can impede water removal from the MEA as well as oxygen diffusion towards the cathode catalyst, a localized increase in electrode substrate porosity may help gain some performance (for example, near the oxidant outlet where water is accumulated). There are a number of ways to achieve this such as using different substrates having unequal porosities and using the more porous material where water accumulation is more acute (use of carbon cloth instead of carbon fiber paper near the oxidant outlet). Another possibility is to modify the carbon fiber paper by decreasing the diffusion path for both product and reactant. This strategy may be achieved, for example, by inserting grooves or holes in the carbon fiber paper in areas where water flooding is more acute. Fig. 4 presents data related to some of these strategies. In each case and at large current densities, the cell performance is higher than a baseline (no substrate modification) because of smaller mass transport losses. The selection of the best approach is also dependent on other factors.

3.3. MEA exposure to excess water or dryness and their effects on lifetime performance

Much less information is available on the behavior of MEAs exposed to an excessive amount of water or subjected to extreme drying conditions [52-56] than for MEA contamination. In addition, the contamination effects cannot be generally dissociated from the long term water exposure effects because details related to impurities are either not disclosed or their importance is not fully recognized.

The thermal stability of ion exchange membranes (Nafion 1100 EW and Dow 560 EW) was previously investigated by others using infrared reflectance absorption spectroscopy and thermal gravimetric techniques in a variety of dry environments (air, N_2 , 95/5 % N_2/H_2) [52-53]. These reports revealed that the ionomer first loses water when heated at low temperatures (above 100 °C) followed by sulfonate site decomposition occurring at around 280 to 300 °C. The decomposition results were not influenced by the presence of Pt or by the environmental composition. Although ionomers are stable under dry environments at normal PEFC operating temperatures, the length of the tests was likely too short

to shed any light on the long term reactivity of ionomers subjected to such conditions. Also, such stability measurements should be duplicated in the presence of water.

Operation of PEFCs without external humidification of the gas streams was recently reportedly carried out for more than 1800 hours [54]. However, no conclusions were presented with respect to material degradation.

Other lifetest data obtained by Wilson et al. over 4000 hours with PEFCs operated at maximum power with overhumidified gases (80 °C cell temperature and respective dew points of 90/105 °C for cathode and anode) [55] revealed that catalyst modification occurs due to particle ripening (crystallite migration particle growth mechanism). The surface area of the catalyst was reduced to different extents for both electrodes (cathode effect was more severe than the anode) and the cathode Pt mass proportion for particles smaller than 3 nm was reduced from 40 to 5 % after 2200 hours. The reason for this effect was attributed to the different levels of hydration existing on both sides of the MEA since it is known that liquids affect the activation energy for particle growth. The wetter environment on the cathode resulted in lower activation energy for particle ripening. Despite this change in catalyst surface area, the PEFC kinetic performance was not affected and this unexpected result can be explained by suggesting that some Pt particles were not active (there is an excess of unused catalyst) and/or the catalyst particle size effect on the oxygen reduction reaction (increase in activity) partially compensates the decrease in catalyst surface area. However, at large current densities, a mass transport loss was observed.

Data obtained over 5000 hours with simulated reformat (80/20 % H_2/CO_2 , 60 °C cell temperature and respective dew points of 65/70 °C for cathode and anode) have also shown the presence of degradation (< 1 % performance loss per 1000 hours) [56]. However, not enough details are provided to ascertain whether or not the degradation is due to the anode kinetics or mass transport (both cathode kinetic and ohmic losses were not affected).

Very little is known of the effects of excessive dryness or wetness on MEA performance. This may be the result of failing to recognize the importance of adequate humidification for prolonged and stable MEA performance. For example, Büchi and Srinivasan data [54] show MEA performance degradation during the lifetest under zero external humidification. Between 150 and 1350 hours the current density at 0.61 V drops from 170 to 130 mAcm⁻². An explanation for the performance loss was not provided and may be attributable to some degradation of the MEA material(s) due to excessive drying.

At Ballard, the effect of long term exposure to excess water was determined by characterizing MEAs before and after soaking them in dionized water (in a teflon lined container) for a defined amount of time without contamination (1000 hours at 80 °C). Fig. 5 illustrates data obtained with two identical MEAs. The polarization curves with oxygen are not significantly modified by the water soak (no kinetic or resistance losses). However, losses

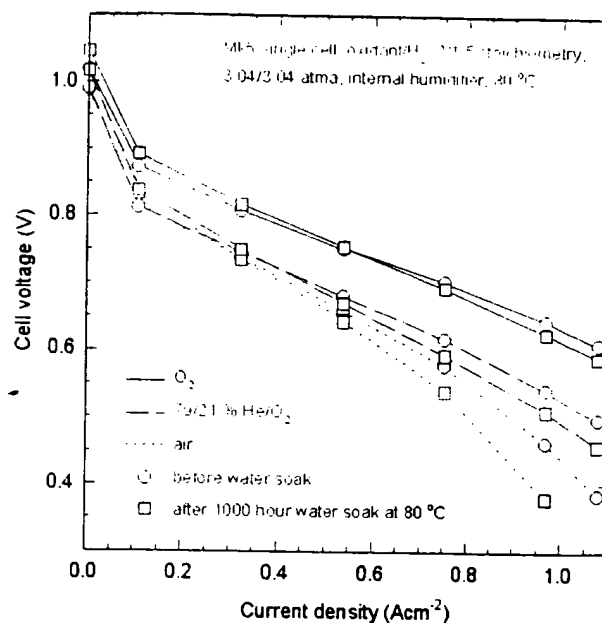


Fig. 5. Effect of an MEA water soak on MEA performance with three different oxidants (oxygen, helox, air)

occur at medium to large current densities for both polarization curves with air and helox (a 79/21 % He/O₂ mixture in which oxygen diffusion is easier than in air thus reducing mass transport losses. The binary diffusion coefficient for an equimolar mixture at 100 °C and 1 atma is 0.307 cm²s⁻¹ for O₂/N₂ but 1.092 cm²s⁻¹ for O₂/He [57]). This is consistent with increased mass transport losses in both the catalyst and the substrate layers (reference [58] contains an explanation of a similar diagnostic technique based on a multicomponent gas analysis). The mass transport loss is consistent with Wilson et al. data [55] and probably with Sishtla et al. data [56]. In both cases the gases were overhumidified which simulates the effect of an extended MEA soak. It is also possible that the degradation described in these references may be due to contaminants since their transport is facilitated by the gas overhumidification. Unfortunately, not enough information is available to separate the effects of the two possible causes of degradation.

The appearance of a mass transport loss is also observed with operating cells and the determination of its origin is further confirmed by comparing data gathered under different water management strategies. For the Mk5 cell, the internal humidifier was designed to provide saturated gases at the cell operating temperature (Mk5 was operated essentially isothermally). With the addition of product water and the decrease in gas flow rates due to consumption, the gas streams are oversaturated along the entire flow field length. In essence, the Mk5 cell experiment simulated the effect of an MEA soaked in water as exemplified by the tests described in the preceding paragraph. In the Mk513 stack, the cell temperature was deliberately increased from the inlet to the outlet port. As a consequence, the additional water produced and the effect of gas consumption on gas relative

humidities is mitigated by the increased amount of water vapor that the streams can carry due to the temperature rise. The fuel cell was operated with less excess liquid water in comparison to the Mk5 cell test. The long term effect of such differences in operation is seen in Fig. 6 which shows lifetest data for both hardware types. Whereas the degradation rate for the Mk5 single cell is $60 \mu\text{Vh}^{-1}$ it is only $1 \mu\text{Vh}^{-1}$ for the Mk513 stack (8 cells) even though the latter was operated at twice the current density of the former (0.538 Acm^{-2}). The main cause of the difference between the degradation rates is due to the relative amount of liquid water present in the cell (both tests were carried out with similar equipment minimizing risks of contamination). For the Mk5 cell, the degradation is mostly due to an increase in mass transport losses (Fig. 7) since there are insignificant changes in cell performance at low current densities (no kinetic loss) and cell resistance (no ohmic loss). The increase in mass transport loss is consistent with the MEA soak experiments, which highlights the need for proper water management to minimize performance degradation. By comparison, for the Mk513 stack and with limited exposure to excess water, the polarization curves obtained initially and after 5000 hours are almost identical (Fig. 8).

The appearance of a mass transport loss is not limited to cases where there is an excess of liquid water within the cell. It is advantageous to reduce humidification requirements so that system complexity is reduced with increased reliability. With fuel cell systems operating on reformat, the air humidification module may be eliminated since the fuel is generally humidified as a result of the reforming process. Data obtained with a Mk513 stack under such conditions are illustrated in Fig. 9. It should be noted that the cell operates with even less liquid water than the case discussed in the previous paragraph (Fig. 6) due to the absence of air humidification. The degradation rate is $24 \mu\text{Vh}^{-1}$

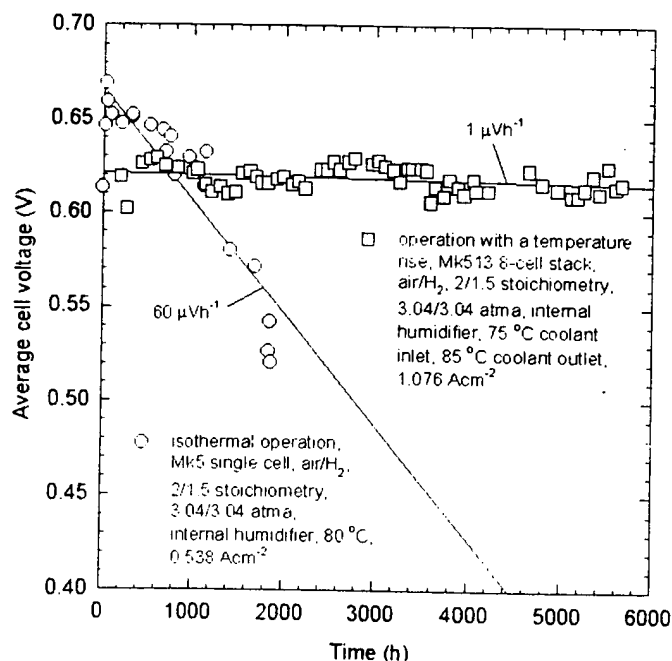


Fig. 6. Effect of hardware design on MEA performance with time.

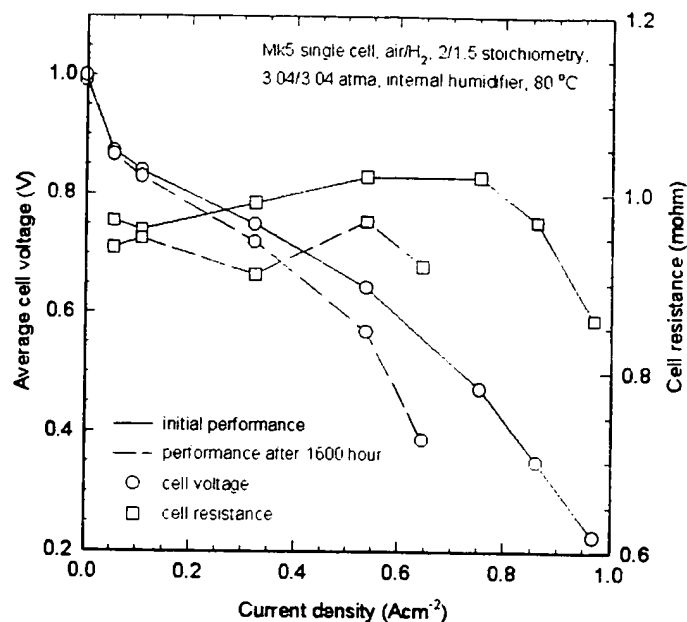


Fig. 7. Effect of operating time on MEA performance and resistance in a Mk5 design

and is largely due to the appearance of a mass transport loss. Table 2 summarizes the differences in cell performance between helox and air, which are indicative of an increase in substrate mass transport loss over time. The appearance of this loss is linked to an improper water balance (relatively too dry). Mitigation techniques are required to decrease this degradation rate to an acceptable level. This could be achieved by modifying the MEA design and should be the subject of continuing studies due to the practical importance of simplified systems operating

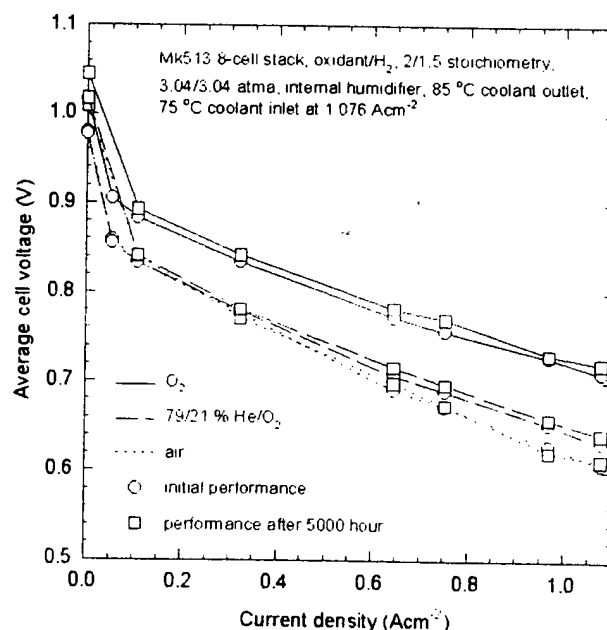


Fig. 8. Effect of operating time on MEA performance in a Mk513 design with three different oxidants (oxygen, helox, air)

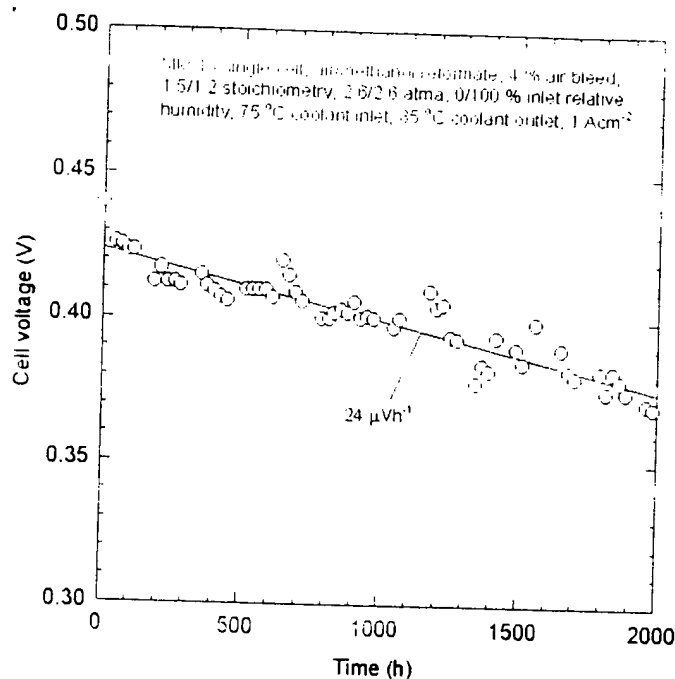


Fig. 9. Effect of operating time on MEA performance in absence of air humidification

Table 2. Mass transport related lifetime characteristics for the cell operated with dry air (Fig. 9)

Operation time (h)	Cell performance difference between helox and air at 1 Acm ⁻² (mV)
0	-8
1000	27
2000	51

with less humidification requirements.

Lifetime data obtained at Ballard and by other groups support the notion that cell degradation due to mass transport is linked to an improper water balance (either too wet or too dry). The use of proper water management techniques is again indicated to maintain a high level of cell performance. Further work is necessary to discern the exact role played by contaminants in such cases and to determine the fundamental reasons behind observed mass transport losses.

4. CONCLUSION

In this paper, the effect of impurities and water management on PEFC performance was investigated. Generally, the conclusions derived from Ballard experimental data were supported by reports produced by other groups such as the appearance of many types of performance losses (cathode and anode kinetic losses, ohmic loss, mass transport loss) due to the presence of contaminants within the MEA and/or PEFC operation over long periods of time. Several areas for further development related to these issues

were also highlighted which include the identification of the MEA contamination modes and related control strategies, the need for more data related to the effects of different water levels within a PEFC on performance degradation and material behavior over long periods of operation, and the elucidation of the fundamental mechanisms leading to a mass transport loss in the presence of improper water management within the PEFC.

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